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(54) Title: BISMUTH CARBOXYLATES AS CATALYSTS FOR CROSSLINKED BLOCKED ISOCYANATE WATERBONE COATINGS				
(54) Titre: BISMUTH CARBOXYLATES UTILISES COMME CATALYSEURS POUR REVETEMENTS RETICULES A BASE AQUEUSE D'ISOCYANATE BLOQUE				
(57) Abstract A catalyst for the crosslinking of a cationic resin with a blocked isocyanate having low environmental toxicity and with activity in waterborne coatings comprises a salt of bismuth and a carboxylic acid with a hydrocarbon chain of from 11 to 36 carbon atoms and a molecular weight of from 165-465.				
(57) Abrégé Cette invention concerne un catalyseur destiné à la réticulation d'une résine cationique avec un isocyanate bloqué qui présente une faible toxicité pour l'environnement et une activité dans les revêtements à base aqueuse. Ce catalyseur comprend un sel de bismuth et un acide carboxylique avec une chaîne hydrocarbonée de 11 à 36 atomes de carbone et un poids moléculaire compris entre 165 et 465.				

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(54) Title: BISMUTH CARBOXYLATES AS CATALYSTS FOR CROSSLINKED BLOCKED ISOCYANATE WATERBONE COATINGS			
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Description

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Bismuth Carboxylates as Catalysts for Crosslinked Blocked Isocyanate Waterborne Coatings

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The present invention is directed to a method of catalyzing the process for de-blocking blocked isocyanates to form crosslinked coatings. More particularly, the present invention relates to the use of certain bismuth carboxylates that are effective in catalyzing both a solvent borne and a waterborne process to form such crosslinked coatings.

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The bismuth carboxylates of the present invention are useful at a very low concentration of 0.05-0.5 wt% of metal based on the total resin weight and are highly effective. This is very desirable in that the emission into the environment of bismuth, a low toxicity metal, is reduced to very low levels.

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BACKGROUND OF THE INVENTION

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Blocked isocyanates have been used in many coating applications, such as powder coatings, electrocoatings, coil coatings, wire coatings, automotive clear topcoatings, stone chip resistant primers, and textile finishes. Traditionally, these coating processes employ organic solvents, which may be toxic and/or obnoxious and cause air pollution. In recent years, the legal requirements for low or no pollution of the environment have led to an increase in the interest in waterborne and high solids coatings.

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In processes wherein blocked isocyanates are used, heating to an elevated temperature is necessary to remove the blocking group from the blocked isocyanate to form free isocyanates. The free isocyanates then react with polyols (polymers containing hydroxy functional groups) to form a crosslinked network as a thin film coating. An obstacle to the use of this process is the high temperature required to remove

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5 the blocking group. The process is extremely slow without a catalyst. It is known that metal compounds such dialkyltin and certain bismuth and zinc salts are excellent catalysts in these solvent borne coating processes. "Crosslinking with

10 5 Polyurethanes." W.J. Blank, ACS Proceedings of Polymeric Materials Science and Engineering (1990) 63:931-935.

15 Bismuth organo-compounds have been used in a variety of processes wherein polyisocyanates or blocked isocyanates is an ingredient. For example, EP 95-109602 describes an epoxide 10 amine adduct with a bismuth compound as being useful in a conventional cationic coating process. US 5,702,581 describes 20 the use of organic bismuth complexes in phosphate dip coating compositions to provide corrosion resistance. The bismuth organic complexes include bismuth carboxylates, such as bismuth 25 lactate. WO 95/29007 disclosed the use of bismuth compounds/mercapto complexes for curing polyisocyanate organic solvent compositions. The bismuth compounds disclosed include bismuth carboxylates, nitrates and halides. WO 96/20967 also 30 described bismuth/zinc mixture with a mercapto complex as a 20 catalyst for producing polyurethane. See also Frisch et al., "Novel Delayed-Action Catalyst/Co-catalyst system for C.A.S.E. 35 Applications", 60 Years Polyurethanes, Kresta et al. ed., Technomic: Lancaster, PA 1998, pp. 287-303. Further, WO 95/08579 described bismuth/mercapto complexes as latent 40 catalysts in a polyol-polyisocyanate adhesive system. The catalyst is described as useful in promoting the rapid cure of the system. The bismuth carboxylates described in these 45 references are those wherein the carboxylate has ten carbons or less in the hydrocarbon structure. These conventional bismuth 30 carboxylates do not provide improved resin performance nor are they effective in water-borne formulations.

50 WO 95/07377 described the use of bismuth lactate in cationic lacquer compositions, which employ urethane reactions.

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A mixture of bismuth and an amino acid or amino acid precursor was disclosed for catalyzing a cationic electrodeposition of a resin film on a metal substrate. The bismuth may be present in the form of nitrates, oxides, trioxides, or hydroxide. DE

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5 19,532,294A1 also disclosed bismuth carboxylates as catalysts for single component polyurethane lacquer coatings in a solvent borne formulation.

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10 Unfortunately, when the known bismuth catalysts are employed in waterborne coatings formulations, it was found that 20 they were not effective. It is suspected that the loss of activity is related to the hydrolysis of the bismuth salt in water. Moreover, even if these compounds function as catalysts in waterborne processes, it has been our experience that a very 25 high level is necessary, usually 10 to 100 times higher than in 15 solvent borne processes. This is undesirable because bismuth has a low degree of toxicity and would cause environmental pollution if a large amount is released into the environment.

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30 Bismuth carboxylates have been used as catalysts in processes that do not involve de-blocking of blocked 20 isocyanates. Bismuth dimethylol propionate has been disclosed in DE 93-43,300,002 as being useful in an electrocoating process 35 for coating phosphate dipped metals to provide anti-corrosion and weather resistance. Bismuth carboxylates are also described in DE 96-19,618,825 for use in an adhesive gel formulation that 40 is safe for contact with human skin. The formulation contains polyether polyols with hydroxy groups, antioxidants, Bismuth(III) C₂-C₁₈ carboxylates soluble in the polyether polyols and OCN(CH₂)₆NCO. JP 95-351,412 describes the use of bismuth neodecanoate as a catalyst for two part adhesive formulations 45 30 containing polyisocyanates, polyols with an ethylenediamine. These formulations do not involve the de-blocking of blocked isocyanates.

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5 For waterborne processes, the catalysts known to be
useful are organo-tin and lead compounds. See WO 95/04093,
10 which describes the use of organo-tin alone or in a mixture with
other compounds including bismuth oxide in a low temperature
15 curing process employing blocked isocyanates. There is no
disclosure of bismuth carboxylates alone as a catalyst for de-
blocking isocyanates. Organo-tin compounds have also been used
in coatings, e.g. in paints for anti-fouling applications.
20 Organo-tin compounds in mixtures with bismuth hydroxy carboxylic
acid salt was described in DE19,613,685. The use of bismuth
lower carboxylates was described as being useful in a phosphate
25 dip process to provide corrosion resistance to lacquer coatings.
The bismuth carboxylates described therein as being useful are
lower carboxylate of bismuth wherein the carboxylic acid has up
30 to ten carbons. The substrate is then coated with an epoxy
resin in the presence of a blocked isocyanate as the
crosslinking agent using a zinc organo compound and/or lead
35 compound as the catalyst. EP0,509,437 disclosed a mixture of a
dibutyltin aromatic carboxylate with a bismuth and a zirconium
40 compound as the dissociation catalyst for electrocoating wherein
a blocked isocyanate is used. Polystannoxane catalysts are also
described in EP0,810,245 A1 as an low temperature catalyst for
45 curing compositions comprising a blocked isocyanate. Bismuth
compounds, including carboxylates were described as being useful
50 as a co-catalyst. However, the process is one in which the
reaction temperature was in the range of 100°C, quite a bit
below the normal temperature of 120°C to 150°C for de-blocking
blocked polyisocyanates. JP 94-194950 described a formulation
for coating materials which are rapidly curable in contact with
55 an amine catalyst vapor or mist. The coating formulation
included polyols, polyisocyanates, antimony or bismuth catalysts
with mercaptans in an organic solvent. The toxicity of both
lead and tin compounds present serious environmental hazards

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The use of solvents in solvent borne processes further result in the undesirable release of toxic and obnoxious chemicals into the environment. For these reasons, the use of organo tin and lead compounds and solvents has been banned in many applications 10 and is highly restricted in electrocoating.

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It is, therefore, important to develop other catalysts or catalysts systems for waterborne processes.

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SUMMARY OF THE INVENTION

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Certain bismuth carboxylates have now been developed 20 as effective catalysts for coatings processes wherein a temperature of at least 130°C is used to de-block blocked isocyanate employed as the crosslinking agent. The bismuth 25 carboxylates of the present invention are compounds wherein the carboxylate is derived from a carboxylic acid with more than ten carbon atoms. The bismuth carboxylates of the present invention have been found to be highly effective and efficient catalysts 30 and are useful at very low concentrations both in solvent and 35 water-borne processes. Thus, even though bismuth has a low toxicity, the low concentrations required reduces the emission of bismuth into the environment and thus reduces environmental contamination.

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An objective of the present invention is to develop 25 catalysts, which are effective, and efficient for de-blocking 40 blocked isocyanate to form crosslinked coatings with reduced environmental contamination.

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It is a second objective of the present invention to 45 develop catalysts, which may be used at very low concentration 30 levels to reduce the emission of toxic substances into the environment.

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It is a further objective to develop a catalyst, which 50 is highly effective not only in solvent borne processes, but

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5 retains its high effectiveness in waterborne coating compositions.

10 It is another objective to reduce the emission of metals into the environment.

15 5 In accordance with the present invention a process has been developed for forming blocked isocyanate crosslinked coatings formulations comprising as a catalyst, a bismuth carboxylate, wherein the carboxylate is derived from a carboxylic acid with a linear or branched hydrocarbon chain of 10 11-36 carbons. The hydrocarbon chain may contain heteroatoms such as nitrogen, oxygen or sulfur. The carboxylic acid may be 20 aromatic or aliphatic, such as: undecanoic, dodecanenoic, palmitic, stearic, oleic, isostearic, abitieic acids. The carboxylic acid may be synthesized or derived from natural fats. 25 15 The catalyst may also comprise a mixture of the carboxylic acids useful in the present invention.

DETAILED DESCRIPTION OF THE INVENTION

30 20 In accordance with the present invention a catalyst for crosslinked blocked isocyanate coatings has been developed. The catalyst comprise a bismuth salt of a hydrophobic carboxylic acid having 11-36 carbon atoms in the hydrocarbon chain and a 35 molecular weight in the range of 165-465. Preferably the 25 carboxylic acid suitable for the present invention is water- insoluble.

40 The carboxylic acid salts of bismuth of the present invention is prepared by heating 1M of bismuth trioxide, Bi_2O_3 , with at least 3M of a carboxylic acid or an anhydride and 45 30 removing the water from the reaction mixture. The reaction is carried out at a temperature of 120-150°C for several hours or until a clear solution is obtained.. The bismuth carboxylates of the present invention are known to be unstable in the presence 50 of water. They are hydrolyzed and break down into their

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constituent parts: bismuth oxide and the carboxylic acid from which they are formed. However, surprisingly, on heating to 130°C, the bismuth carboxylate reforms and is highly effective as a catalyst.

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5 This catalyst is also effective in solvent borne coatings, which contain low levels of water, such as in pigmented coatings. Furthermore, the bismuth carboxylates of the present invention are stable and have a longer shelf life.

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10 The catalytic activity of the bismuth catalysts useful in the present invention can be maintained if the salt is prepared from a hydrophobic, carboxylic acid having 11-36 carbons in the hydrocarbon chain. The hydrocarbon chain may comprise non-carbon atoms, such as nitrogen, oxygen or sulfur. The carboxylic acid may be aromatic or aliphatic with a 15 molecular weight in the range of 165-465. The carboxylic acids useful in the present invention are water-insoluble. In a water-borne electrocoating process, the cationic resin co-deposit with the hydrolyzed bismuth carboxylate of the present 20 invention as a mixture of bismuth oxide and carboxylic acid.

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When heated to a curing temperature of 130°C or above, the bismuth carboxylate forms *in situ* to catalyze the process.

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The carboxylic acid salts of bismuth may be prepared by heating one mole of bismuth trioxide (Bi₂O₃) with at least 3 moles of a carboxylic acid or an anhydride and removing the 40 25 water formed. The reaction is carried out at a temperature of 120-150°C for 1 to 5 hours or until a clear solution is obtained. The bismuth carboxylate catalysts of the present invention are effective in both solvent borne and water borne 45 coatings. It is particularly useful in pigmented coatings.

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30 The bismuth carboxylates of the invention may be used singly or in combination as mixtures. To form a mixture of the carboxylates, a mixture of carboxylic acids or anhydrides may be

5 used in the process. The carboxylates may also be prepared in situ, i.e. a mixture of a bismuth salt such as bismuth oxide or chloride with carboxylic acid, singly or in mixtures may also be 10 incorporated into the coating formulation.

15 5 Cationic water-borne resins or cationic electrocoating resins useful in this invention can be typically prepared by reacting a bisphenol A type epoxy resin with an epoxy equivalent weight of between 200 to 2000, preferably between 400 to 1000 with an amine. The amine can be ammonia, a secondary, primary 10 or a tertiary amine. If ammonia is used in the preparation of the cationic resin, the reaction of the epoxy resin with ammonia 20 has to be conducted in the presence of large excess of free ammonia to suppress gelation of the resin. In this reaction a combination of primary, secondary and tertiary amine functional 25 15 resin is formed. With primary amines, depending on the ratio of amine to epoxy secondary, and tertiary amine functional resins are formed. With secondary amines tertiary amine functional resins are produced. If an excess of epoxy is used and if the 30 reaction is conducted in the presence of some water and 20 neutralizing acid, there is also the potential for the formation of quaternary ammonium group containing resins.

35 35 Another way to prepare cationic resins is by co-polymerization of cationic monomers such as dimethyl-amino-propyl-methacrylate, dimethyl-amino-ethyl-methacrylate, 40 25 dimethyl-amino-propyl-acrylamide or t-butyl-amino-ethyl-acrylate with an acrylic or methacrylic ester monomer or optionally with styrene or acrylonitrile. Other methods are the reaction of 45 30 anhydride functional polymers with amines with primary or secondary and t-amine groups and a mono epoxide compound as shown in US 3,984,382.

50 50 If a waterborne formulation is desired, an alcohol or a polyol can be solubilized or dispersed in water in the

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presence of nonionic groups or a nonionic surfactant. The alcohol or polyol may be incorporated in the bisphenol epoxy resin itself. For example, a bisphenol epoxy resin can be reacted with a methoxy-polyethylene glycol or a methoxy-polyethylene-ether-amine with a MW of between 500 to 2000.

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Waterborne resin formulations suitable for this invention may also include resins dispersed in water in the presence of a nonionic surfactant. An epoxy or an acrylic or polyester resin may be dispersed in water. The nonionic groups can be a part of the resin structure or a part of an external surfactant. Commercial products, which are suitable, include a dispersion in water of solid bisphenol A glycidyl resins with a molecular weight of between 900 to 4000.

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The blocked isocyanate crosslinker useful in this invention are aromatic or aliphatic isocyanates with a blocking group, which can be removed. Often the de-blocking to the isocyanate is a displacement reaction, wherein the blocking group is displaced with another group. Typical blocking groups for the isocyanate are selected from the group consisting of malonates, triazoles, ϵ -caprolactam, phenols, ketoxime, pyrazoles, alcohols, glycols, glycol ethers and uretdiones.

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Some typical di or polyisocyanates suitable for the invention are: hexamethylene diisocyanate, isocyanurate trimer, biuret, isophorone diisocyanate, tetramethylxylylidine diisocyanate and methylene bis(phenyl isocyanate). Typical examples of blocking groups are methyl ethyl ketoxime, ϵ -caprolactam, 1,2,4-triazole, 3,5-dimethylpyrazole, phenol, 1,2-ethylene glycol, 1,2-propylene glycol, 2-ethylhexanol, 2-butoxyethanol, 2-methoxy (2-ethoxy ethanol).

30 The cationic resins suitable for the invention may also be typically dispersed in water in the presence of a suitable water soluble organic acid such as formic, acetic,

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5 glycolic or lactic acid or an inorganic acid such as sulfamic acid.

10 A coating formulation is normally prepared by blending and dispersing the blocked isocyanate crosslinker, the cationic 5 resin and the catalyst of this invention in water. If pigments are added they can be dispersed separately in the resin. If 15 neutralization of the cationic resin with an organic acid is required, the acid can be added to the resin or to the water phase. Usually high shear dispersers are used to emulsify or 10 disperse the resin.

20 The catalyst of this invention is also advantageous for use in solvent borne coating formulations. Most pigmented 25 formulation have shown a decrease of catalytic activity on aging. This reduction in catalyst activity is attributable to 15 the presence of water on the surface of the pigment. Based on experience, it is known that catalyst deactivation takes place if the coating formulations are cured at high humidity. 30 Although the catalyst of the present invention is predominately suitable for waterborne or water-dispersed coatings. It would 20 be advantageous to use a catalyst with a long shelf life in solvent borne coatings, such as a catalyst of the present 35 invention .

40 The present invention further includes a coating formulation comprising of polyol, a blocked isocyanate 25 crosslinker and a bismuth carboxylate catalyst. The coating formulation can contain varying amounts of water, depending on 45 the desired application. The bismuth carboxylates of the present invention is a salt of bismuth and a carboxylic acid with a total of between 11 to 36 carbons or a mixture of bismuth 30 oxide or chloride with a carboxylic acid with a total of between 11 to 36 carbons. The carboxylates of the present invention are soluble in a water-immiscible solvent.

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The present invention is further directed to a cationic electrocoating formulation comprising a water-dispersible cationic polyol, a blocked isocyanate and a bismuth catalyst of the present invention.

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5 The water-dispersible cationic polyol is at least di-functional, preferably tri functional or higher. The blocked isocyanate is present at a molar ratio sufficient to facilitate crosslinking. The bismuth catalyst is used at a concentration of between 0.01 to 0.5 weight percent (wt%), preferably between 10 0.1 to 1.0 wt%, of metal based on the total resin solids in the 20 formulation.

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The catalyst may also comprise a bismuth salt, such as an oxide or chloride and not a carboxylate, in combination with a free carboxylic acid to form the bismuth carboxylate of the 15 present invention in situ. The bismuth carboxylate may be made from a single or a mixture of carboxylic acids.

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Typical carboxylic acids suitable for the present invention are selected from the group consisting of linear and branched, saturated and unsaturated, aromatic and cycloaliphatic 20 C₁₁ to C₃₆ mono and di carboxylic acids. Examples of suitable carboxylic acids include undecanoic, dodecanenoic, palmitic, 35 stearic, oleic, isostearic, abetieic acid, etc. These acids can be derived from natural fats or produced synthetically.

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The present invention further include coating 25 compositions comprising a polyol, a blocked isocyanate and a bismuth salt of a water insoluble aliphatic, cycloaliphatic or aromatic, carboxylic acid with a total number of carbons in the hydrocarbon chain of between 11 to 36. Optionally, the chain 30 may contain heteroatoms such as oxygen, nitrogen or sulfur. The catalyst of the present invention also includes blends of bismuth salts, such as bismuth oxides and chlorides with the

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5 above acids, or a mixture of the bismuth carboxylates as defined
above.

10 The bismuth carboxylate of the present invention is
added to the resin blend at a concentration of between 0.01 to
5 1.0 wt%, preferably between 0.05 to 0.5 wt%, of bismuth metal
based on the total resin weight in the formulation. Preferably
15 the resin is in a waterborne cationic electrocoating formulation
system.

20 The following examples are provided to illustrate the
10 present invention and are not meant to limit the scope thereof.

25 Example 1

15 Preparation of a Cationic Bisphenol A Glycidyl resin

25 A cationic resin was prepared by reacting a
diglycidylether bisphenol A resin with a secondary amine in
accordance with the following formulation.

		Equivalent Weight			
			Weight	M	Ratio
30	Bisphenol A epoxy	117.3	540	0.217	1
35	Diethanolamine	22.8	105	0.217	1
	2-butoxyethanol	29.4			

40 A commercially available bisphenol A-epichlorohydrin
20 epoxy resin with an epoxy equivalent weight of 540 were
dissolved in 2-butoxyethanol and blended with the diethanolamine
(1 equivalent of amine). The reaction mixture was heated to
80°C for 3 hours and then held over night. The mixture is
adjusted with 2-butoxyethanol to approximately 83 wt% solids.

45 25 This is a cationic resin, which can be dispersed in water.

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Example 2Blocked Isocyanate Crosslinker

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5 A polymeric aromatic methylene phenyl isocyanate with an average functionality of 2.5 was reacted with an equivalent amount of 2-methoxy(2-ethoxyethanol) until FT-IR showed a complete disappearance of the NCO groups.

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		<u>Weight</u>	<u>Equivalent weight</u>	<u>M</u>	<u>Ratio</u>
20	MDI, polymeric	42.4	131	0.324	1.0
	2-methoxy(2-ethoxyethanol)	39.6	120	0.33	1.02

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Example 3Preparation of the coating

15 169 parts by weight of the cationic resin of example 1 was blended with 82 parts by weight of the crosslinker of Example 2 and 14.1 parts by weight of a 85 wt% solution of lactic acid in water. A catalyst selected from the following table and added to the mixture in an amount as indicated in the 30 table. 352 parts by weight of de-ionized water was added under high speed agitation to the blend. The blend was permitted to 35 age for 24 hours prior to application. Films were cast on 20 pretreated steel panels at a dry film thickness of 15 micron and 40 baked for 20 minutes at 180°C.

	<u>Catalysts</u>	<u>Metal wt% on total resin</u>	<u>MEK double rubs</u>
45	No catalyst	0.0	<10
	Dibutyltin dilaurate	0.25	10
	Dibutyltin dilaurate	0.50	10

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	Bismuth tris (2-ethylhexanoate)	0.25	100	
10	Bismuth tris (2-ethylhexanoate) + 3 M isostearic acid *	0.25	200 200 (after 48 hours)	
15	Bismuth tris (2-ethylhexanoate) + 1.5 M dimeric fatty acid *	0.25	200 (after 48 hours)	

* corresponds to 3 equivalent of COOH per Bi and the dimeric fatty acid is a C₁₈ dimeric acid derived from tall oil.

20 The test results on the coating formed from this formulation clearly illustrates the superior performance of a 5 bismuth carboxylate catalyst in the presence of a non-volatile acid during the baking process.

25 Example 4

10 A cationic resin was prepared from a diglycidyl ether of bisphenol A in accordance with the following formulation.

30		Equivalent			
		Weight	weight	M	Ratio
	Bisphenol A epoxy	166.3	875	0.19005	1
35	Diethanolamine	18	105	0.17142	0.9
	2-butoxyethanol	67			

40 A commercially available bisphenol A-epichlorohydrin epoxy resin with an epoxy equivalent weight of 875 is dissolved in 2-butoxyethanol and blended with the diethanolamine (0.90 45 equivalent of amine). The reaction mixture is heated to 80°C for 3 hours and then held over night. The mixture is adjusted with 2-butoxyethanol to approximately 73 wt% solids.

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Example 5

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5 A blocked isocyanate crosslinking agent was prepared
 in accordance with the formula in the following table. MDI
 10 polyisocyanate was reacted with 2-butoxy(2-ethoxyethanol) at
 15 100°C for 4 hours.

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		Equivalent <u>Weight</u>	<u>Weight</u>	<u>M</u>	<u>Ratio</u>
	MDI, polymeric	51.8	131	0.395	1
	2-butoxy(2-ethoxyethanol)	66.6	162	0.411	1.04

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Example 6

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Ccating Formulation

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25 1 part by weight of the cationic resin of example 4
 was blended with 118 parts by weight of the crosslinker of
 example 5 and with 11.5 parts by weight of a 85 wt% solution of
 15 lactic acid in water. 618 parts by weight of de-ionized water
 was added under high speed agitation to this blend. The
 20 formulation was aged for 24 hours before application. Films were
 cast on pretreated steel panels at a dry film thickness of 15
 25 micron and backed for 20 minutes. All catalyzed formulations
 were formulated with the corresponding catalyst at a
 concentration of 0.25 wt% metal based on the total resin blend.
 The catalyst was added to the formulation prior to the addition
 30 of water. The coating was applied on phosphate pretreated
 steel, 15 μ film thickness.

25 Solvent resistance Methylethylketone double rubs

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<u>Catalyst\Cure Temp., 20 min.</u>	<u>180°C</u>	<u>170°C</u>	<u>165°C</u>
None	10	10	10
Dibutyltin dilaurate	63	30	10

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5	Bismuth tris(2-ethyl-hexanoate)	150	70	20
10	Bismuth tris(2-ethyl-hexanoate) and 3M of isostearic acid	200	150	20
15	Bismuth tris(2-ethylhexanoate) + 1.5M of oleoyl sarcosine	200	150	70

15 This formulation illustrates the substantial improvement in cure response over dibutyltin dilaurate and bismuth 2-ethylhexanoate with 8 carbons. It also illustrates 20 that not only simple carboxylic acids but also a complex acid such as a sarcosine may be combined with bismuth to provide improved cure performance.

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10 Example 7

30 2-butoxyethanol blocked isocyanate

A polymeric MDI isocyanate is blocked with 2-butoxyethanol. No catalyst was used in the following reaction.

	MDI polymeric	Equivalent		
		Weight	weight	M
35	MDI polymeric	55.0	131	0.395
	2-butoxyethanol	70.7	162	0.411

40 15 The polymeric MDI was mixed with the 2-butoxyethanol and held at 100°C for 4 hours.

45 20 Example 8

Coating Formulation

322 parts by weight of the cationic epoxy resin of Example 4 was blended with 125 parts by weight of the 2-

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butoxyethanol blocked MDI crosslinker of Example 7. 12.9 parts by weight of lactic acid and 589 parts of de-ionized water were added to this blend. The catalyst was added before the addition of water. The formulations with catalyst contained a catalyst level, which corresponded to 0.25 wt% metal based on the total amount of binder (resin and crosslinker). The water was added under high speed agitation.

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The coating formulations were cast on iron phosphate pretreated steel and cured for 20 minutes at the indicated temperature. The dry film thickness was 30 micron. Solvent resistance was measured as methyl ethyl ketone double rubs.

	<u>Aging Period</u>	<u>24 hrs</u>	<u>1 week</u>	<u>5 days, 0.6 mils thickness</u>	<u>5 days</u>
25	Cure temp, °C	180	180	180	170
30	No catalyst	10	10	10	10
35	DBTDL	200	80	50	50
40	Bismuth tris(2-ethylhexanoate)	200	200	100	50
45	Bismuth tris(2-ethylhexanoate) and 3M of isostearic acid	200	200	200	120
	Bismuth tris(2-ethylhexanoate) and 3M of oleyl sarcosine	200	200	180	50
	Bismuth tris(2-ethylhexanoate) and 1.5M of octadecyl succinic acid			200	50

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Example 9Screening of Potential Catalysts

10 5 Other known catalysts for alcohol blocked isocyanates were screened in an acrylic polyol and a MDI polyisocyanate blocked with butyl carbitol formulation. The ratio of blocked isocyanate to hydroxyl was 1/1.

		Catalyst Me wt%	MEK double rubs	MEK double rubs
20	Cure temperature, °C		150°C	170°C
	No catalyst	0	2	2
25	Dibutyltin dilaurate	0.18	10	130
	Bismuth tris(2-ethylhexanoate)	0.18	120	200
	Zn bis(2-ethylhexanoate)	0.18	24	200
30	Al chelate	0.18	20	
	Zr chelate	0.18	11	
	Ti tris(ethyl acetoacetate)	0.18	13	
35	Zr bis(2-ethylhexanoate)	0.18	10	
	Mn Naphthenate	0.18	10	
	Ca bis(2-ethylhexanoate)	0.18	10	
40	Co bis(2-ethylhexanoate)	0.18	100	
	Cr tris(2-ethylhexanoate)	0.18	15	

10 45 As shown in this screening study only bismuth tris(2-ethylhexanoate), DBTDL and Zn bis(2-ethylhexanoate) showed any promise of improved performance.

Example 10Comparative Example

5 A bismuth lactate catalyst was prepared according to Feola et. al. (PCT Int. Application WO 9507377). A bismuth dimethylol-propionic salt catalyst was prepared according to Foedde et. al. (Eur. Pat. Appl. EP 690106). A bismuth catalyst 10 was also prepared from an amino acid (glycine) according to Bethoski et. al. (PCT Int. Appl. WO 9810024).

	<u>Formulation</u>	<u>Parts by Weight</u>
20	Epoxy resin of Example 4	251.3
	Blocked isocyanate crosslinker of Example 5	118.4
25	Catalyst	0.25 wt% metal on total resin solids
	Lactic acid 25 wt% solution in water	11.5
30	De-ionized water	618.8
	Total Formulation	1000.0

Water-based cationic E-coat formulations were prepared by mixing the epoxy-amine adduct and the blocked isocyanate, with various catalysts respectively into each of the resins 15 blends. Each of the formulations was neutralized with lactic acid to pH 5.0 to 6.0. The resin formulation was then 40 emulsified with water to 30 wt% solids content

The formulations containing the different catalysts were applied after 24 hours on Bonderite 1000 steel panels 20 pretreated with iron phosphate. The cured coatings were evaluated for solvent resistance (methylethylketone double rubs), humidity, corrosion and impact resistance. The results obtained demonstrated the advantage of the catalyst of the

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5 present invention over other bismuth carboxylate catalysts at
the same metal concentration. The catalyst of the present
invention provides a faster cure rate and better humidity
resistance than the comparative catalyst examples. The test
10 5 results clearly illustrate the superior cure behavior in
improved solvent and humidity resistance provided. The catalyst
of the present invention provided less blistering at a lower
15 cure temperature than the catalysts of the present art.

Solvent resistance (MEK double rubs)

10 Catalyst amount: 0.25 wt% metal on total resin solids
Cure time : 20 minutes
Substrate : Bonderite 1000 (pretreated cold rolled steel)
Dry film thickness: 0.85 mil

	<u>Cure temp, °C</u>	<u>165</u>	<u>170</u>	<u>175</u>	<u>185</u>	<u>190</u>
25	No catalyst	5	5	5	20	190
	Bismuth tris(isostearate)	80	125	200	200	200
30	Bi tris(lactate)	75	85	200	200	200
	Bi tris(dimethylol- propionate)	50	82	185	200	200
35	Bi tris(glycinate)	5	22	50	90	200

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Catalyst\Cure temp, °C	170	180
	Gloss 20°% t blister	Gloss 20°% t blister
No catalyst	0.6	100
		45.0 45.0

		21			
5	Bi tris(isostearate)	93.6	25	92.7	0
10	Bi tris(lactate)	81.0	60	83.1	0
15	Bi tris(dimethylol-propionate)	52.5	80	89.8	0
20	Bi tris(glycinate)	2.9	95	54.9	50.0

Example 11

15 A coating formulation was prepared according to the formulation in Example 10.

20 5 Dry film thickness : 0.6-0.8 mil
 Catalyst amount : 0.25 wt% metal on total resin solids
 Substrate : Iron phosphate pretreated steel.

	<u>Catalysts\</u> <u>Cure temp °C</u>	<u>190</u>	<u>185</u>	<u>180</u>	<u>175</u>	<u>170</u>
25	No catalyst	90	20		5	5
30	DBTDL			63		30
35	Bi tris(stearate)			200		150
40	Bi tris(2-ethylhexanoate) + 3M Neodecanoic acid			200	120	70
45	Bi tris(2-ethylhexanoate) + 3M lauric acid		200	185	70	

Claims

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What we claim is:

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1. A method of catalyzing a cationic coating process with a blocked isocyanate as the crosslinking agent wherein the catalyst is selected from the group consisting of a mixture

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5 of a salt of bismuth selected from the group consisting of bismuth oxide, bismuth chloride and a carboxylic acid having a hydrocarbon chain of 11 to 36 carbons and a molecular weight in the range of 165-465 and a bismuth carboxylate wherein the carboxylate has a hydrocarbon chain of 11 to 36 carbons and a molecular weight in the range of 165-465.

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2. A method according to Claim 1 wherein the salt of bismuth and the carboxylic acid is water insoluble.

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3. A method according to Claim 1 wherein the bismuth carboxylate is water insoluble.

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4. A method according to Claim 1 wherein the salt of bismuth and a carboxylic acid is a mixture of bismuth and at least two carboxylic acids.

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5. A method according to Claim 1, 2, 3, or 4 wherein the carboxylic acid is selected from the group consisting of undecanoic, dodecanoic, palmitic, stearic oleic, isostearic and abitieic acids.

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6. A method according to Claim 4 wherein the salt of bismuth and a carboxylic acid is a mixture of bismuth tris(2-ethylhexanoate) and a second carboxylic acid, isostearic acid.

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7. A method according to Claim 4 wherein the salt of bismuth and a carboxylic acid is a mixture of bismuth tris(2-ethylhexanoate) and a second carboxylic acid, a fatty acid selected from the group consisting of oleyl sarcosine and octadecyl succinic acid.

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8. A cationic coating formulation comprising a blend of:
a) a cationic resin selected from the group consisting of

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5 i) an epoxy-amine reaction product: a bisphenol A type epoxy resin with an epoxy equivalent weight of between 200 and 2000 and an amine selected from the group consisting of a primary amine, a secondary amine and a tertiary amine;

10 5 ii) an epoxy-polyol reaction product: a bisphenol A with an epoxy equivalent weight of between 200 and 2000 and type resin and a polyol selected from the group consisting of glycols and glycol ethers;

15 10 iii) copolymers of cationic monomers selected from the group consisting of dimethyl-amino-propyl-methacrylate, dimethyl-amino-ethyl-methacrylate, dimethyl-amino-propyl-acrylamide and t-butyl-amino-ethyl acrylate with an acyclic or methacrylic ester monomer optionally with styrene or acrylonitrile;

20 15 b) a blocked isocyanate crosslinker selected from an aromatic and an aliphatic isocyanate with a blocking group selected from the group consisting of malonates, triazoles, ϵ -caprolactam, phenols, ketoxime, pyrazoles, alcohols, glycols and glycol ethers;

25 20 c) optionally a polyol, a methoxy-polyethylene glycol and optionally an alcohol, a methoxy-polyethylene-glycol-ether-amine having a molecular weight in the range of 500 to 2000;

30 25 d) 0.01 to 1.0 wt% metal based on the total weight of the cationic resin blend of a bismuth catalyst selected from the group consisting of:

35 30 i) bismuth carboxylate, a salt of bismuth and a carboxylic acid having a hydrocarbon chain of 11-36 carbons, a molecular weight in the range of 165-465;

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ii) a mixture of bismuth oxide with a carboxylic acid having a hydrocarbon chain of 11-36 carbons, a molecular weight in the range of 165-465;

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iii) a mixture of bismuth carboxylates wherein the carboxylic acid has a hydrocarbon chain of 11-36 carbons, a molecular weight in the range of 165-465.

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9. A cationic coating formulation according to Claim 8 the carboxylic acid is selected from the group consisting of undecanoic, dodecanoic, palmitic, stearic oleic, isostearic and abitieic acids..

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10. A cationic coating formulation according to Claim 8 wherein the bismuth catalyst is a mixture of bismuth tris(2-ethylhexanoate) and a second carboxylic acid, isostearic

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15 acid.

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11. A cationic coating formulation according to Claim 8 wherein the bismuth catalyst is a mixture of bismuth tris(2-ethylhexanoate) and a second carboxylic acid, a fatty acid selected from the group consisting of oleyl sarcosine and octadecyl succinic acid.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/03490

A. CLASSIFICATION OF SUBJECT MATTER		
IPC(7) :C08F 20/34; C08G 59/14; C08K 03/20; C08L 33/14, 63/02, 75/12 US CL :523/415; 524/555; 525/124, 528; 528/49, 55 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) U.S. : 523/415; 524/555; 525/124, 528; 528/49, 55		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WEST 2.0 (Databases USPT, DWPI, JPAB, EPAB). Search terms: (poly or di)isocyanates or (poly)urethanes, and bis(meth) carboxylates.		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category ^a	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 810245 A1 (ELF ATOCHEM NORTH AMERICA, INC.) 12 MARCH 1997, page 4, LINES 1-4; page 5, lines 13-14, 17, 20 and 24 and page 6, lines 55-56.	1-3, 5, 8 and 9
Y	EP 509437 A1 (KANSAI PAINT CO. LTD.) 21 October 1992, page 2, lines 46-47; page 4, lines 42-43; page 6, lines 54-58 and page 7, Table 1, Sample No. 9.	1-3, 5, 8 and 9
Y	US 5,021,598 A (PATNAIK et al.) 04 June 1991, column 3, lines 7-22, 31-33 and 37-38; and column 8, lines 30-31.	2-6, 9 and 10
Y	JP 04-065417 A (YOKOHAMA RUBBER CO. LTD.) 02 March 1992 (02.03.92), abstracts.	2-7 and 9-11
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "B" earlier documents published on or after the international filing date "C" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reasons (as specified) "D" document referring to an oral disclosure, use, exhibition or other means "E" document published prior to the international filing date but later than the priority date claimed		** later document published after the international filing date or priority date and not in conflict with the application but used to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "Z" document member of the same patent family
Date of the actual completion of the international search 25 MAY 2000	Date of mailing of the international search report 22 JUN 2000	
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer ROBERT SELLERS Telephone No. (703) 308-0661	

INTERNATIONAL SEARCH REPORT

International application No. PCT/US00/03490

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,584,362 A (LECKART et al.) 22 April 1986, column 1, line 63 to col. 2, line 7 and columns 4-6 table.	2-5 and 9
Y	US 4,786,655 A (GROGLER et al.) 22 November 1988, column 2, lines 4-16 and 41-54.	2, 3, 5 and 9
Y	US 4,868,266 A (MECKEL et al.) 19 September 1989, column 2, lines 7-27 and column 4, line 66.	2, 3, 5 and 9
Y	JP 05-155962 A (YOKOHAMA RUBBER CO. LTD.) 04 December 1991 (04.12.91) abstract.	2, 3, 5 and 9
Y	JP 03-091520 A (YOKOHAMA RUBBER CO. LTD.) 17 April 1991 (17.04.91), abstract.	2, 3, 5 and 9
Y	JP 10-218962 A (NIPPON POLYURETHANE KOGYO KK) 18 August 1998 (18.08.98), abstracts.	2, 3, 5 and 9

Form PCT/ISA/210 (continuation of second sheet) (July 1998)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/03490

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.: because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

The additional search fees were accompanied by the applicant's protest.
 No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/03490

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claims 1-7, drawn to a method of catalyzing a cationic coating process with a blocked isocyanate crosslinking agent and a bismuth catalyst.

Group II, claims 8-11, drawn to a cationic coating formulation comprising a cationic resin, a blocked isocyanate crosslinker, an optional polyol and a bismuth catalyst.

The inventions listed as Groups I and II do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: The special technical feature is the combination of a blocked isocyanate crosslinking agent and a bismuth catalyst. European Patent No. 509,437 (KANSAI PAINT) (page 2, lines 46-47 and page 4, line 42) discloses a mixture of a blocked isocyanate and salts of bismuth and organic acids along with a dialkyl tin aromatic carboxylate. The claimed combination does not make a contribution over the prior art, thereby confirming the lack of unity of invention.

This application contains claims directed to more than one species of the generic invention. These species are deemed to lack Unity of Invention because they are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for more than one species to be searched, the appropriate additional search fees must be paid. The species are as follows:

The bismuth catalysts comprising:

- 1) The mixture of bismuth oxide and a C_{11} - C_{24} carboxylic acid within the bismuth catalyst genus of claim 1.
- 2) The mixture of bismuth chloride and a C_{11} - C_{24} carboxylic acid within the bismuth catalyst genus of claim 1.
- 3) The bismuth carboxylate within the bismuth catalyst genus of claim 1.
- 4) The mixture of bismuth and at least two carboxylic acids of claims 4 and 5 from undecanoic, dodecanoic, palmitic, stearic, oleic, isostearic and abietic acids wherein the number and species of carboxylic acids within the mixture are identified.
- 5) The mixture of bismuth tris(2-ethylhexanoate) and isostearic acid of claim 6.
- 6) The mixture of bismuth tris(2-ethylhexanoate) and oleyl succinate of claim 7.
- 7) The mixture of bismuth tris(2-ethylhexanoate) and octadecyl succinic acid of claim 7.

The cationic resins of claim 8 comprising:

- i) An epoxy-amine reaction product.
- ii) An epoxy-polyol reaction product.
- iii) Copolymers of cationic monomers wherein the cationic monomers are selected from dimethylamino (propyl or ethyl) methacrylate, dimethylaminopropyl acrylamide or t-butyl-aminoethylacrylate and the comonomers are selected from a (meth)acrylic ester, styrene and/or acrylonitrile.

The claims are deemed to correspond to the species listed above in the following manner:

The bismuth catalyst: claims 1-11.

The cationic resin: claim 8.

Claims 1-11 are generic.

The species listed above do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, the species lack the same or corresponding special technical features for the following reasons: The special technical feature is the combination of a blocked isocyanate crosslinking agent and a bismuth catalyst. European Patent No. 509,437 (KANSAI PAINT) (page 2, lines 46-47 and page 4, line 42) discloses a mixture of a blocked isocyanate and salts of bismuth and organic acids along with a dialkyl tin aromatic carboxylate. The claimed species of bismuth catalysts and cationic resins do not make a contribution over the prior art, thereby confirming the lack of unity of invention.

